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## PATENT SPECIFICATION 18,818/70

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Complete Specification  
entitled (50) PROCESS FOR THE PRODUCTION OF ETHYLENE  
OXIDE

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The following statement is a full description of the invention, including the best method of performing it known to us:

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R. S. Adams, Standard Priority, Catalog

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The present invention relates to a process for the production of ethylene oxide by catalytic oxidation of ethylene.

The preparation of ethylene oxide by oxidation of ethylene in the presence of suitable catalysts is well known.

These known processes can be divided into two groups, in the first one the oxidation is carried out in the presence of air, in the second one in the presence of pure oxygen.

In both cases use is made of catalysts known in the art as "silver catalysts": metallic silver is in fact the element that promotes the oxidation of ethylene to ethylene oxide.

It is also known that in the preparation of these silver catalysts may be deposited on suitable supports and in order to improve their activity.

A known industrial process for producing ethylene oxide comprises reacting a mixture containing ethylene in the range from 1 to 30%, preferably from 2 to 10%, and oxygen (or air) in the range from 2 to 3%, on a silver catalyst bed at a temperature from 150 to 400°<sup>0</sup> and at a pressure in the range from 0.7 to 35 atmospheres. To overcome low yields an inhibitor is used, for example an halogenated organic compound for instance dichloroethane. Contact times ranges generally from 0.1 to 15 seconds.

We have now surprisingly found out that it is possible to accomplish a very profitable industrial process if a very concentrated ethylene feed is allowed

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to contact a silver catalyst, as hereinafter described.

According to the present invention there is provided a process for the oxidation of ethylene to ethylene oxide with pure oxygen or a mixture containing oxygen at a temperature ranging from 100 to 400°C and at a pressure ranging from 0.7 to 35 atmospheres comprising reacting ethylene at a concentration of from 40 to 80% in the presence of a catalyst constituted by Ag, O<sub>2</sub> and Ba, the ratio between the gram atoms of Ag and the sum of gram atoms of calcium and barium being equal to or greater than 1.

The most preferred ethylene/oxygen ratio in the feed is higher than 3.

With reference to the catalyst employed in the process of the present invention it is not possible to utilize all known catalysts; some of them have little activity and present low selectivity; a general but not limitative criterion for the choice of the catalyst may be based on the fact that the best catalyst seems to be the ones having as active part silver and other compounds and/or elements as pure metals, metalloids, halogens or their compounds known for affecting oxidation reaction.

The elements and/or compounds which promote the ethylene oxide formation reaction are alkaline earth metals such as calcium and barium. Such elements and/or compounds can be supported on a carrier and, if the support is alumina, it should have a good porosity to allow the active part (Ag, Ca and Ba) to be well distributed and fixed thereon.

Catalyst can be used as powder too, that is the active part only (e.g. for fluidized beds) without support.

Preparations of catalysts according to the present invention are illustrated in the examples.

The process of the present invention shows that an increase of ethylene concentration causes a corresponding

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increase of selectivity and, contrarily to what generally is cited in literature, a reaction velocity decrease.

When the oxidation operation is carried out with the ethylene concentration of the present invention it is usually noticeable that the material constituting the reaction equipment, saturated hydrocarbons possibly present in the feed or rare gases present have little or no detrimental effect on the present process. Thus control of the reactants is usually only necessary to provide good results. In fact it has been found carbon dioxide need not be precluded from the process of the present invention. This is surprising as at low ethylene concentrations (i.e. below 1%) carbon dioxide has an undesirable effect on the catalyst activity.

Acceptable levels of inert for example as saturated hydrocarbons and rare gases such as carbon dioxide is 7% to 60% of the gaseous mixture, preferably between 1% and 50% and most preferably at least 20%.

It has been also surprisingly found that ethane has little or no detrimental effect on the present process. Conflicting statements have been made in the prior art as to the presence of ethane in the production of ethylene oxide. In U.S. Patent 3,119,657 it is stated that hydrocarbons should be withdrawn from the feed mixture while French Patent 1,555,797 states ethane from 4 to 40% by volume of the feed mixture can be present without undesirable effects. Thus it is not clearly apparent why in the present process ethane can be present without incurring disadvantages. Perhaps the only factors which may affect the situation are the ethylene concentration and

the catalyst used. 18,818/0

With regard to the catalyst used in the present invention the catalyst comprises silver, calcium and barium such that the gram atom ratio of silver to calcium plus barium is at least one. Preferably the gram atom ratio of silver to calcium plus barium is 4 to 15. Most preferably the gram atomic ratio of Ag/Ca/Ba is 13/2.5/1.

In the preferred embodiment of the present invention the active part that is silver, calcium and barium is supported on a carrier. For this purpose ceramic carriers such as alumina can be employed. When alumina is used it must have a suitable porosity and preferably be macroporous.

Another important factor is the preparation techniques of these compositions.

The best technique consists substantially in preparing a solution of water soluble salts in water, said salts being constituted by metals of the active part of the catalyst, precipitating said metals in the solution so as to obtain a powder of active part, preparing a suspension of this powder, treating the carrier with said suspension and finally drying and heat treating the catalyst obtained.

The use of high ethylene concentration in the feed simplifies the operating cycle and allows, as before mentioned, to accomplish ethylene oxide production in very advantageous conditions.

A simplified flow-scheme of the process according to our invention is represented in fig. 1 where to a reactor 1 containing silver catalysts, ethylene and oxygen or mixture containing oxygen are sent through line 2; ethylene and oxygen or mixture containing oxygen are

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introduced through inlets 3 and 4 respectively; from the reactor 1, a mixture containing ethylene oxide and unreacted compounds are withdrawn. Said stream is sent to the tower 5 where the ethylene oxide is absorbed while unreacted compounds are withdrawn from the top of tower 5 and partially recycled, because of their high ethylene content, directly to the reactor 1 through lines 6. The other part said unreacted compounds are sent to tower 8 where the ethylene is scrubbed and where a  $\text{CO}_2$  and inert gases purge is provided; the ethylene recovered in 10 is recycled to reactor 1 through line 9.

Through inlet 7 water for removing ethylene oxide is introduced.

Between tower 5 and 8 an intermediate stage, e.g. to scrub  $\text{CO}_2$ , and also several oxidation reactors and other conventional equipment known in the art may be provided.

The process according to our invention allows to obtain high selectivity values increasing with the ethylene concentration; furthermore because of the higher limits of the concentration range (namely 40-80%) this process allows to operate, if it is convenient, -unlike conventional known processes - without inhibitors. Thus an important advantage is achieved because the ethylene oxide leaving the reactor does not contain undesirable impurities.

When the operation is carried out in presence of an inhibitor, this can be chosen in the wide class of the compounds known in the art for this purpose as, for instance, the halogenated cyanohic compounds and among

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then dichloroethane is suggested. Practically no limits for the amount of employed inhibitors are considered in the process according to the present invention.

By way of example the amounts of inhibitor are usually lower than 0.5 ppm by volume in the whole gaseous mixture and preferably between 0.01 and 0.3 ppm. However higher concentrations, up to 10-30 ppm, may be employed.

Other advantages arise due to the fact it is possible to eliminate the  $\text{CO}_2$  scrubber required by prior art processes. Also as stated previously it is not usually necessary to remove ethane from the feed mixture. This allows for improvement in operating costs as special feeds and consequential equipment are not required.

If it is noticed that ethane does begin to accumulate in the process it can always be removed by the purge.

A further advantage is that it is possible to operate with oxygen contents even higher than 5% and up to the explosivity limits of the mixtures and it improves the plants productivity.

Another remarkable advantage is that with the same productivity the process according to our invention can operate at a temperature lower than in conventional processes; the temperature may reach even 30°C and sometime lower values, extending in this way the catalysts life. Therefore in the process according to our invention the reaction temperature ranges from 100 to 400°C.

The present invention will now be further illustrated by the following examples.

The tests of the examples have been carried out

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by gas-chromatography.

EXAMPLE

Some tests have been carried out at constant temperature and at several ethylenes contents in the feed with a 5/16" catalyst prepared in the following way:

100 grams of silver nitrate, 21 grams of tetrahydrate calcium nitrate and 21 grams of barium nitrate were dissolved in 1500 cc of deionized water (Ag/Ca/Ba ratio is 25/2.5/1).

The obtained solution, which may be opalescent because of the presence of small traces of silver chloride that may form, was filtered with adsorbents.

62 grams of anhydrous sodium carbonate

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were dissolved in 500 cc of distilled and purified water with 2 grams of silver nitrate.

The obtained solution was filtered.

Before mixing the two said solutions, a small amount of calcium chloride (about 10 mgs) was added to the nitrate solution.

The coprecipitation of silver calcium and barium carbonates was carried out adding, under rapid mixing, the sodium carbonate solution to the nitrates solution.

Precipitation of the carbonates in a very subdivided form was obtained. Said solution was filtered and the precipitate washed with deionized water and dried in a stove, in presence of a small air flow, for some hours at a temperature of 110°C.

About 120 grams of catalytic powder were obtained, said powder was finely milled in a hammer mill then the milled catalytic powder was sprinkled on the carrier.

The carrier was a commercial one, e.g. aluminum having the following characteristics:

(Alumina S.A. 5218 by Norton):

Shape: 5/16" diameter Spheres

Composition:

$\text{Al}_2\text{O}_3$  65.50  $\text{TiO}_2$  0.10  $\text{Fe}_2\text{O}_3$  0.03

$\text{SiO}_2$  12.40  $\text{MgO}$  0.60  $\text{K}_2\text{O}$  0.50

$\text{Fe}_2\text{O}_3$  0.00  $\text{CaO}$  0.40

Physical characteristics (X Ray):  $\beta - \text{Al}_2\text{O}_3$

+ Mullite

Porous structure; porosity by volume = 50.0%

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pores radii = 100 - 700 microm

This carrier presented a porous structure particularly suitable for the purpose, as it allowed to obtain a complete penetration of the catalyst even into the inner parts of the spheres.

Of course other types of alumina or of carrier presenting the same properties could be used.

The inhibition was carried out mixing the obtained catalytic powder with 800 gram of a 30% ethylene glycol solution and treating the obtained suspension with 550 grams of carrier kept under stirring to facilitate a uniform inhibition.

The obtained matter was dried and activated under controlled air flow, at about 350°C, for some hours.

Said catalyst, for the execution of the cited tests, has been put in a reactor having a 1" *length* and a 1" diameter, kept at constant temperature by bottom jacket stirred by nitrogen flow.

The operating conditions were the following:

Pressure : atmospheric  
 Temperature : 171°C  
 Catalyst amount : 484 grams, 9,9% of Silver  
 Flow rate : 210 ml/hr  
 Contact time : 4.6. sec

The results of the tests were:

No. of the test	%C <sub>2</sub> H <sub>6</sub> in feed	reaction velocity ml/Sec	Selectivity %	T°C
1	5	60	129	63
				171
				452,754

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2	5	60	60	74	172
3	3	71	55	76.5	172

EXAMPLE 2

In the same reactor, at the same operating conditions (except for the temperature) and <sup>measuring</sup> use of the same catalyst described in example 1, tests have been carried out at constant reaction velocity, varying the ethylene concentrations and at increasing temperature.

The results obtained were the following one :

No. of the tests	T°C	50 <sub>2</sub> feed	50 <sub>2</sub> % feed	Reaction velocity	Selectivity % moles
				moles of C <sub>2</sub> H <sub>4</sub> reacted/	
				M <sup>3</sup>	
1	153	5	5	55.60	57
2	160	3	40	55.60	71.5
3	166	5	60	55.60	76.5
4	171	5	77	55.60	76.5

EXAMPLE 3

A series of tests has been carried out in a stainless steel reactor having an inner diameter of 16 mm. and a length of 28 cm provided with an outer jacket wherein a silicon oil, as thermostatic fluid, circulated. The employed catalyst was constituted by a Ag, Cu, Bi carbonates powder prepared as described in example 1 and calcined at 300°C in air flow. The operating temperature and pressure have been kept respectively at 155°C and 1 atmosphere.

The tests have been carried out by loading the reactor with 24.5 grams of catalyst (height of catalyst bed = 14.5 cm.) and feeding to the reactor

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5 lit/hr. of gaseous mixtures containing 5% of  $O_2$  and from 7% to 60% of ethylene.

The contact time was of 12.6 seconds.

The results of the test were the following:

No. of the  $^{\circ}C$  test %  $O_2$  %  $O_2C_2H_4$  feed reaction velocity  
test % moles  
of  $O_2C_2H_4$   
reacted/hr.

1	5	32	1.50	73.6
2	5	43	1.30	74.9
3	5	60	0.78	77.4

For 7% ethylene concentration the selectivity was about 62% and for 22% of ethylene it did not exceed 70%.

EXAMPLE 4

In the same reactor and with the same catalyst of example 3, a series of test with different concentrations of ethylene and keeping constant the reaction velocity, by means of the temperature, has been carried out.

The fed mixtures had a constant content of oxygen of about 5% while the ethylene concentration ranged between 7% and 50%; the contact time was of 12.6 seconds, as in example 3.

The obtained results were the following:

case:  
No. of the  $^{\circ}C$  test %  $O_2$  %  $O_2C_2H_4$  reaction velo- Selectivity  
smoles  $O_2C_2H_4$  % moles  
reacted/hr.

1	173.5	5	32	3.70	67.6
2	178	5	43	3.67	69.2
3	183	5	60	3.73	71.0
4	188	5	73	3.75	73.2
5	189	5	83	3.76	73.4
			12		4.52754

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The selectivity increased from about 57% for feed ethylene concentration of 7%, not exceeding any how 62% when the ethylene concentration was about 20%.

## EXAMPLE 1

To control the influence of the material with which the reactor was built, two series of tests have been carried out with the same catalyst and with ethylene concentration ranging between 40% and 60%. In these series of tests the same stainless steel reactor of example 1 and an iron reactor with the same geometric dimensions had been employed. The employed catalyst is similar to the one described in the example 1. The obtained results of the tests carried out in the stainless steel reactor were:

No. of test	% CO <sub>2</sub> feed	% C <sub>2</sub> H <sub>4</sub> feed	reaction velocity moles C <sub>2</sub> H <sub>4</sub> reacted/20	Selectivity % moles
1	17%	5	40	201,3
2	17%	5	60	72,8
3	17%	5	77	53,1

The results of the test carried out in the iron reactor were:

No. of test	% CO <sub>2</sub> feed	% C <sub>2</sub> H <sub>4</sub> feed	reaction velocity moles C <sub>2</sub> H <sub>4</sub> /20	Selectivity % moles
1'	17%	5	40	90,0
2'	17%	5	60	63,6
3'	17%	5	77	53,5

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EXAMPLE 6

For checking the influence of ethane on the reaction, a test has been effected with 60% ethylene, 2% of O<sub>2</sub>, 10% of ethane, 25% of N<sub>2</sub>; this test has been compared with a test effected with 60% of ethylene, 2% of O<sub>2</sub> and 35% of N<sub>2</sub>.

Both tests have been carried out in the same reactor and at the same operating conditions of example 1; also the catalyst is similar to the one described in example 1.

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The results of the test were the

following:

- test without ethane:
  - temperature = 175°C
  - reaction velocity = 80.3 moles reacted  $C_2H_4/m^3$ /hr.
  - selectivity = 73.6% moles.
- test with 10% of ethane:
  - temperature = 175°C
  - reaction velocity = 89.1 moles reacted  $C_2H_4/m^3$ /hr.
  - selectivity = 72.6% moles.

**EXAMPLE 7:**

For checking the influence of argon on the reaction two tests have been carried out in the reactor, with the catalyst and at operating conditions described in the example 1; the concentrations of the two tests were:

- 1) 60%  $C_2H_4$  - 35  $O_2$  - 5%  $N_2$
- 2) 60%  $C_2H_4$  - 35  $O_2$  - 5% Ar.

Both tests have been carried out at 172°C.

The obtained results for the reaction velocity and selectivity were:

	reaction velocity $C_2H_4$ reacted/m <sup>3</sup>	selectivity % moles
Mixture 1)	79.1	74.1
Mixture 2)	79.4	73.8

In a test in which nitrogen or argon have been replaced by carbon dioxide at the same concentration, the obtained selectivity was substantially equal to the selectivity of the tests with nitrogen or carbon dioxide.

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EXAMPLE 6

Preparation of the catalyst  
For this example use has been made of techniques of  
example 1.

A precipitation or a co-precipitation in  
form of carbonates of the elements constituting the  
active part has been carried out starting from the  
corresponding solutions of nitrates or of other water  
soluble salts. Carbonates were so obtained in an  
extremely subdivided state and were filtered, washed  
with deionized water and dried in a stove in a weak  
air flow for some hours at a temperature of about  
110°C.

Said materials were then deposited on  
the carrier. As carrier use was made of the alluvium  
of example 1; said alluvium had the following character-  
istics:

Shape : 5/16" diameter spheres  
physical chemistry characteristic (X Ray)  $\alpha\text{-Al}_2\text{O}_3 + \text{Illite}$   
Porous structure; porosity by volume = 50.0%  
Pores radii = 100 - 700 microm

The impregnation of the active part was realized  
preparing a suspension of said part in mixture water/  
ethylene glycol and treating the carrier with this  
suspension.

Then the obtained material was dried in  
a controlled air flow at a temperature of about 350°C  
for some hours. With this technique the catalysts numbered  
from 1 to 9 have been prepared.

With reference to table 1 the catalyst

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numbered 6 this is an example of separated precipitation  
on one hand Ag and on the other hand the two promoters  
(Ca and Na) and mechanical mixing of the precipitate  
while for the catalysts 7,8 and 9 little amounts of  
CaCO<sub>3</sub>, generally about 5.10<sup>-4</sup> gr. per Ag gr., have been  
added.

In all said catalysts the Ag content is 10%  
by weight of the finished catalyst.

Variants of this preparation are those in  
which the preparation of precipitates different from  
carbonates are provided; for instance the precipitation  
in form of oxides or the inhibition without using  
polyacrylic acids, as for instance a ethylacrylic  
glycol, or also the replacement of the operation of  
co-precipitation with a precipitation of the single  
constituents followed by a mechanical mixing of all the  
precipitates.

Another series of catalysts has been  
prepared with the solution technique.

It consists in preparing an organic salt of  
the silver and of the possible promoters (preferably  
lactates are prepared) and in impregnating the carrier  
with said solutions; during the operation the temperature  
was kept at about 90 - 95°C with variable durations  
according to the type of carrier and anyway not longer  
than one hour; afterward the solution was withdrawn and  
the impregnated material was kept at 90 - 95°C for about  
15 minutes.

The catalyst was then put in a stove for  
12 hours at 70 - 80°C in a weak air flow; then it was

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calcined at 320°C for about 5 hours in a controlled  
air flow.

With this technique the catalysts numbered  
from 10 to 15 have been prepared.

All the catalysts from 1 to 15 have been  
employed for the production of ethylene oxide with  
feeds containing either 5% to 60% of ethylene  
and 5% of oxygen. The results of the tests are  
shown in table 1 where possible variants of the  
compositions of the feed mixture are indicated.  
The tests have been carried out in a conventional  
reactor having a 1 m length, a 1" diameter kept at  
constant temperature by a dothorn jacket kept in  
agitation by a nitrogen flow and in a such way to  
have the same productivity i.e. the same number of  
moles of ethylene reacted per catalyst unit volume  
and per hour.

Practically the productivity was kept at a  
rate of 180 - 200 moles of ethylene per liter of  
catalyst per hour.

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Table 1

Catalyst No.	Atomic ratio Ag/Co/Be	1 (desorption)		% vol.	Carrier	Silver, % by weight			
		2 (deactivation)							
		5% C <sub>2</sub> H <sub>4</sub>	60% C <sub>2</sub> H <sub>4</sub>						
1	25/0/0	46 <sup>180</sup>	67 <sup>190</sup> 77 <sup>220</sup>		55/15% spheres of Al <sub>2</sub> O <sub>3</sub> + 10% porcelain 50-55 pt volume pores radius 100 + 700 microns	20			
2	25/0/1	47 <sup>166</sup>	67 <sup>173</sup> 75 <sup>185</sup>						
3	25/2/50	46 <sup>166</sup>	70 <sup>170</sup> 76 <sup>180</sup>						
4	25/25/1	(a) 251 40 <sup>151</sup>	74 <sup>163</sup> 78 <sup>172</sup>						
5	25/0/35	45 <sup>168</sup>	65 <sup>169</sup> 73 <sup>177</sup>						
6	25/3.5/0	42 <sup>170</sup>	72 <sup>203</sup>	67 <sup>176</sup> 74 <sup>198</sup>					
7 (a)	25/0/0	(a) 220 30		65 <sup>197</sup> 71 <sup>212</sup>					
8 (a)	25/0/1	62 <sup>199</sup>		61 <sup>199</sup> 70 <sup>209</sup>					
9 (a)	25/0.5/0	(a) 90 60		66 <sup>279</sup> 72 <sup>185</sup>					
10	200/0/1	(a) 26 35		57 <sup>222</sup>	CARB. 3/25% by CARBO- BONDON CO.	24.6			
11	24/0/1	52 <sup>195</sup>		47 <sup>201</sup> 65 <sup>219</sup>	Carbon dust, g pores 50 + 2504	24.7			

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12	24/0/0				(a) 62 <sup>196</sup>	Allumina LADS by Norton pores = 2 μ total porosity 0.46 cc/g	24.5
13	15/2.5/2	35 <sup>192</sup>	(b) 60 <sup>215</sup>	57 <sup>204</sup>	66 <sup>203</sup>	Allumina 3/16" pores 50-650 total porosity 0.25 cc/g	8
14	24/0/1	35 <sup>199</sup>	60 <sup>244</sup>	52 <sup>209</sup>	61 <sup>212</sup>	Extruded cylinder Allumina 5 2 mm Length 5 mm pores 5-154-304 total porosity 0.18 cc/g	19.1
15	14/0/1	34 <sup>195</sup>	52 <sup>250</sup>	58 <sup>205</sup>	61 <sup>205</sup>	Allumina 3/16" pores 5-50-230/4 total porosity 0.05 cc/g	8

(\*\*) carriers with different porosity may be suitably employed.

in table 1 we have

8 Selectivity scales %

750 reaction temperature

- (a) test effected with a mixture of 26 O<sub>2</sub>, 6.3% CO<sub>2</sub>, 68%
- (b) test effected in presence of 0.03 ppm of inhibitor
- (c) catalyst prepared with CaCl<sub>2</sub>
- (d) test effected with a mixture containing 0.24 ppm of inhibitor.

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EXAMPLE 9

To a reactor made of carbon steel, kept at constant temperature with downdown and operating at a pressure of 18 kg/cm<sup>2</sup>, several mixtures have been fed whose compositions are indicated in table 2. The table shows the operating temperatures and the obtained results. The other operating conditions have been the same in all the tests so as to make possible a confrontation of them. Further the catalyst employed in the tests indicated in table 1 is the same of example 1.

TABLE 2

$\text{NO}_2\%$	$\text{NO}_x\%$	$\text{NO}_3\%$	$T^\circ\text{C}$	reported $\text{NO}_x\%$ mole/mole	Selectivity index %
4.9	4.0	—	216	7.1	71.7
5.0	4.2	10.4	205	6.8	62.8
20.3	4.0	—	209	7.1	75.3
20.2	4.1	10.0	207	7.2	74.7
39.4	4.1	—	213	6.8	76.2
40.1	4.1	10.3	215	7.0	74.7
39.4	3.9	—	233	10.5	72.3
40.4	4.0	10.7	233	10.0	72.6
40.1	4.0	—	243	11.3	69.5
39.7	4.0	10.7	233	11.3	67.8
40.2	10.3	10.8	234	13.4	69.4
40.7	4.0	—	253	12.2	66.5
40.8	4.1	10.8	243	12.2	67.3

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In each test, beside the indicated components, dichloroethane was fed, as inhibitor, at a concentration of 0.03 ppm by volume with respect to the mixture; the remainder were inert, above all nitrogen. The obtained results clearly showed the following trend: at low ethylene concentration (about 5%) the presence of ethane deeply decreased the selectivity; said effect decreased with increasing ethylene concentrations till practically to vanish for ethylene concentration of about 40%.

#### EXAMPLE 10

In a stainless steel reactor, kept at constant temperature with downdra and operating at a pressure of 18 kg/cm<sup>2</sup>, seven catalysts have been tested. The ones numbered from 1 to 6 in table 3 were similar to the ones described in example 1; the one numbered 7 was of the type described in U.S.P. 2,477,435.

The mixture compositions are given in table

3.

Beside the cited components also dichloroethane as inhibitor at a concentration of 0.03 ppm by volume with respect to the mixture was fed, the remainder were inert and especially nitrogen.

The other operating conditions were identical in all the tests so as to make them confrontable.

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Table 3

Catalyst no.	%C <sub>2</sub> H <sub>4</sub>	%CO <sub>2</sub>	%O <sub>2</sub>	%C <sub>2</sub>	reacted C <sub>2</sub> H <sub>4</sub> mMole/m	Selectivity value %
1)	5,1	0	4,0	218	7,5	72,1
2)	5,3	50,3	4,0	213	5,8	66,1
3)	40,0	0	4,0	215	7,0	76,5
4)	40,1	10,0	4,0	218	7,1	75,9
5)	40,1	50,0	4,0	219	7,1	73,6
6)	40,1	50,5	4,0	223	7,2	73,6
7)	40,0	50,2	4,1	246	7,0	69,6

The tests showed the following trends:  
at low ethylene concentration (about 5% the presence  
of CO<sub>2</sub> deeply decreased both the activity and the  
selectivity of the catalyst; said negative effects  
decreased remarkably and acceptably for 40% of  
ethylene.

*The word "Dowtherm" is registered  
as a Registered Trade Mark.*

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The claims defining the invention are as follows:-

1. A process for the oxidation of ethylene to ethylene oxide with pure oxygen or a mixture containing oxygen at a temperature ranging from 100 to 400°C and at a pressure ranging from 0.7 to 35 atmospheres comprising reacting ethylene at a concentration of from 40 to 80% in the presence of a catalyst constituted by Ag, Ca and Ba, the ratio between the gram atoms of Ag and the sum of gram atoms of calcium and barium being equal to or greater than 1.
2. A process according to claim 1 in which the ethylene/oxygen ratio is higher than 3.
3. A process according to claim 1 in which the ratio between the gram atoms of Ag and the sum of gram atoms of Ca and Ba is in the range of from 4 to 15.
4. A process according to claims 1 and 3 wherein the Ag/Ca/Ba gram atomic ratio is 15/2.5/1.
5. A process according to claims 1, 3, 4 wherein the catalyst is supported on porous alumina having a spheric shape, pores radii ranging from 100 to 700 microns, a volume porosity of about 50%, and the following composition:  
 $\text{Al}_2\text{O}_3$  55.50;  $\text{TiO}_2$  0.10;  $\text{NO}_2$  0.03%;  
 $\text{SiO}_2$  12.40;  $\text{MgO}$  0.60;  $\text{K}_2\text{O}$  0.50;  
 $\text{Fe}_2\text{O}_3$  0.20;  $\text{CaO}$  0.40; and said porous alumina by X-ray analysis shows an alumina-mullite structure.
6. A process according to any one of claims 1 to 5 wherein said catalyst is supported on a ceramic carrier.
7. A process according to claim 5 or 6 wherein the catalyst supported on a carrier is one which has been prepared by preparing an aqueous solution comprising silver, calcium and barium salts, precipitating silver, calcium and

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barium metals from said aqueous solution, preparing a powder of said precipitated silver, calcium and barium metals, preparing a suspension of said powder, distributing said powder on a carrier and drying the powder on said carrier.

8. A process according to any one of the preceding claims wherein said oxidation is carried out in the presence of ethane.

9. A process according to claim 8 wherein the ethane is present in a concentration of up to 5%.

10. A process according to claim 9 wherein the ethane is present in a concentration up to 3%.

11. A process according to any one of the preceding claims wherein the oxygen is in a concentration from 0% up to explosive limits.

12. A process according to any one of the preceding claims wherein carbon dioxide is present in a concentration of 7% to 60%.

13. A process according to any one of the preceding claims wherein an inhibitor is present.

14. A process according to claim 13 wherein the inhibitor is an organic halogenated compound.

15. A process according to claim 14 wherein the inhibitor is present in an amount less than 0.3 ppm.

16. A process according to claim 15 wherein the inhibitor is present in an amount ranging from 0.01 to 0.3 ppm.

17. A process according to claim 1 as herein described with reference to the Examples.

18. A process according to claim 1 as herein described with reference to the drawing.

19. Ethylene oxide when produced by the process defined

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in any one of the preceding claims.

DATED: 20th August, 1978

SHAN PROQUETI S.P.A.  
By its Patent Attorneys:  
PHILLIPS CANNON AND FIFIELD

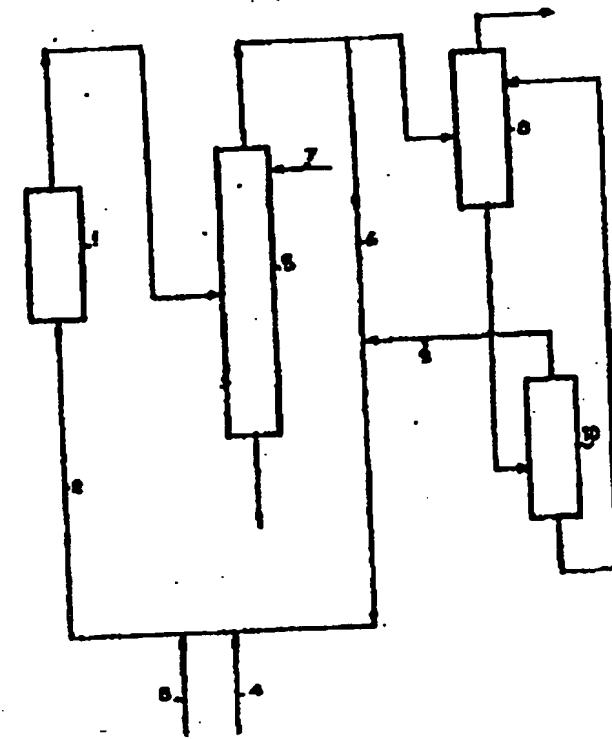
*David P. Tiffenbach*



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